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Evaluation of Conceptual Flowsheets for Incorporating LWR Fuel Materials in an Advanced Nuclear Fuel Cycle

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ORNL/TM-11466

CHEMICAL TECHNOLOGY DIVISION

EVALUATION OF CONCEPTUAL FLOWSHEETS FOR INCORPORATING LWR FUEL MATERIALS IN AN ADVANCED NUCLEAR FUEL CYCLE

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EXECUTIVE SUMMARY

A preliminary study and an evaluation have been made by a group of experts at ORNL of possible reprocessing flowsheet options and process steps for recovery of actinides from Light Water Reactor (LWR) fuel. These actinides could be used for fuel in a Liquid Metal Reactor (LMR), and, at the same time, for transmutation of the wastes to less hazardous materials. It may also be necessary to remove and isolate a few other long-lived radionuclides from the spent fuel. Principally because of the much more extensive technology base, the evaluation showed that flowsheets based on PUREX and TRUEX solvent extraction are the only processes assured of successful operation and suitable for near-term application; they therefore provide the Low-Technological-Risk (LTR) Case. Within this case, the options for handling the actinide elements must be further examined to appropriately optimize the interface between the LWR recovery plant and the fast reactor recycle facility. The judgement reached in this study was that the approach with the greatest assurance of technological success was (1) to recover plutonium and neptunium decontaminated from fission products, convert them to a metal alloy, and fabricate fuel for transport to the reactor site and, (2) to recover the remaining actinides and lanthanides in a TRUEX process, convert them to oxides, and ship this product to the reactor facility for incorporation in recycle metal fuel. A similar alternative with high assurance of technological success would blend the remaining actinides and fission products with the plutonium and neptunium before they leave the reprocessing plant, either before or after the oxide reduction step.

Many alternative flowsheets including non-aqueous routes were examined within the criteria defined for the study. Four of these warrant further examination. The first two are closely related options, which are based on PUREX technology, but have simplified process steps that produce a purified uranium product and a fission product/actinide oxide product. A pyro-process would then be used to convert the fission product/actinide product to a metallic actinide product. A third, more speculative non-aqueous process that is based on molten salt technology and would require extensive development, is also included. The fourth approach would use fluoride volatility technology.

No new economic evaluation for these processes could be done within this limited study. Prior studies indicated that the cost of facilities for recovery of the actinides from PUREX waste streams would increase the cost over conventional reprocessing by about 42%. A careful integration and optimization of the flowsheets in a combined facility, using LTR technology, would probably reduce the incremental costs to a range of 25% or less. Other costs associated with actinide recovery/transmutation may be as significant as this added cost for actinide recovery.

A very preliminary assessment of the R&D needs for the aqueous-based processes identified three critical areas requiring development: (1) modifications to PUREX to provide for routing a major portion of the neptunium with the plutonium product, a tactic already being examined in France, or to quantitatively recover a separate neptunium product; (2) further development and testing of TRUEX with actual high-level waste streams from PUREX; and (3) further development of processes for converting the actinide nitrate solutions to metal for reactor fuel. R&D on the options for conversion appears warranted to permit further process and economic comparisons. The alternative aqueous processes require detailed flowsheet analyses to understand any potential advantages and to further define R&D needs. The non-aqueous processes need flowsheet analyses and extensive chemical experiments to determine feasibility. The technical uncertainties associated with the chloride flowsheet (flowsheet 4) are significantly greater than for the fluoride volatility flowsheet.

No attempt was made to define actinide recovery goals for this study nor to make recovery efficiencies a criteria in comparing options. Some examination of prior work both revealed the complexity of determining the goals and provided some insights towards useful approaches. These insights included: (1) the importance of neptunium and the merit in routing it to the plutonium product (unless it is to be recovered as a separate product), (2) the high recoveries required for the LMR fuel reprocessing, and (3) a perspective that recoveries that are achievable with known technology (assumed to be no better than 99.8%) might provide an adequate goal for this program. Higher recoveries would require additional treatment of waste streams and secondary wastes (HEPA filters, cladding hulls, fuel residues, etc.). A follow-on comprehensive assessment of this is required that would examine a broad range of factors, such as (1) practical recoveries from normal process steps, and (2) methods for (and costs of) further special treatment of waste streams for added recovery and decrease in repository risks for all cases.

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ABSTRACT

A preliminary study by a group of experts at ORNL has generated and evaluated a number of aqueous and non-aqueous flowsheets for recovering transuranium actinides from LWR fuel for use as fuel in an LMR and, at the same time, for transmutation of the wastes to less hazardous materials. The need for proliferation resistance was a consideration in the flowsheets. The current state of development of the flowsheets was evaluated and recommendations for additional study were made.

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1. INTRODUCTION

An evaluation has been made of possible process steps and combined flowsheets that have potential for use in recovering the actinides from LWR fuel and converting them into a form suitable for fuel in the Integral Fast Reactor (IFR). The driving force for this evaluation is the removal of the actinides from the LWR fuel to reduce its potential radioactive risk during long-term waste storage. Such an approach also provides the plutonium necessary for startup of IFR reactors and may provide partially enriched uranium to an enrichment process. Transmutation of the actinides in the fast reactor removes them from the waste repository scenario.

The scope of this effort is given in Appendix A. Conversations with Terry Johnson (Argonne National Laboratory) indicate that a separate process may be needed to convert the oxide product to a metallic or chloride form before introduction into the standard IFR processes. The uranium content should be reduced by a factor of 10 to 20. The criteria used for judging the various processes were (1) safety, (2) waste acceptability, (3) suitability of the process for its intended use, and (4) the adequacy of the existing technology base. Several meetings were held by the participants to generate process steps and flowsheets and to discuss their advantages and disadvantages. This is the final version of the report following outside reviews.

In these evaluations several ground rules have been assumed:

1. This study does not examine any of the steps involved in the IFR processes, beyond obtaining information regarding the requirements for feed material to the system.

2. Since the requirements for the degree of recovery of transuranium actinides from the LWR fuel have not been set, the evaluation did not critically examine the flowsheets relative to the degree of actinide removal achievable. Some thoughts on establishing the required degree of recovery are given in Appendix D.

3. It is recognized that, in addition to the actinides, a number of fission products contribute either to the long-term potential risk or to a near-term risk. Studies have addressed techniques for recovering these materials in aqueous and pyro-processing. The current evaluation has not examined recovery of these materials in detail; a brief discussion is given in Appendix E.

4. This study assumes a clean uranium product is required from the LWR reprocessing plant. There are several reasons for this assumption: (1) the cost difference in production of a relatively dirty uranium product and a clean product is likely to be small. Uranium is the dominant material by weight in an LWR reprocessing plant. Savings in avoidance of cleanup of uranium product may be wiped out by the higher cost to remotely solidify, convert to other chemical forms, and package the uranium product; (2) if uranium is a waste, a contaminated uranium will have high disposal costs; (3) clean uranium may be a valuable product, since its fissile assay exceeds natural uranium. It can be the feed for an enrichment process to produce recycle uranium for LWRs. It can also be a direct feed to heavy water reactors; and (4) if dirty uranium is stored for recycle into LMRs, the cost of storing a highly contaminated, radioactive material for decades will become significant. There may also be major licensing difficulties. Current regulations require that if spent fuel is reprocessed, the waste must be treated, solidified, and packaged shortly after being generated. It is relatively easy in a technical, economic, and regulatory context to store clean recycle uranium. Long-term storage of highly contaminated uranium faces major unknowns. Lastly, the owner of the LMR fuel reprocessing plant may prefer cheap, easy-to-transport, easy-to-store, depleted, clean uranium bought on the open market even if dirty uranium is "free."

2. EVALUATION OF PROCESS STEPS, AND FLOWSHEET AND PRODUCT-FORM OPTIONS

2.1 PROCESS STEP OPTIONS

Process steps were evaluated by the criteria developed, and discussions of the process steps that were evaluated are given in Appendix B. Most steps were eliminated either because potential advantages were limited or there were reasons to believe the technology was not suitable for this application. The process steps that were most favored were:

1. Use a mechanical shear to expose the fuel.

2. Dissolve the fuel from the sheared cladding with nitric acid.

3. Recover and decontaminate the uranium and plutonium from the fuel solution using solvent extraction by tri-n-butylphosphate (PUREX).

4. Use TRUEX (or a modification thereof) to recover transplutonium actinides and lanthanides from other materials.

5. Use direct thermal denitration or precipitation of oxalate followed by calcination to produce oxides from the nitrate solution. The choice of process depends on what materials are being converted to oxides, but direct thermal denitration is favored where applicable.

6. Convert the oxides to metal suitable for fabrication into IFR fuel.

Other process steps which may be promising, but would require significantly more development are:

7. Use high-temperature oxidation/nitriding to destroy the cladding.

8. Volatilize the Zircaloy as $ZrCl_4$.

9. Voloxidize and agitate to remove the fuel from sheared or perforated cladding.

10. Dissolve the fuel in a molten chloride salt using carbon and chlorine.

11. Separate the uranium by pyro-processes.

12. Separate the other materials using pyro-processes.

13. Separate the uranium by fluoride volatility.

14. Convert the halides to metals or metal alloys using pyro-processes.

The first five process steps lead to aqueous processes that are variations of the current PUREX process. The sixth step would use one of the processes developed for plutonium or uranium metal production. The seventh step is an alternative method for disrupting the fuel cladding to expose the fuel for further processing. The eighth to fourteenth (and final) process steps would constitute a pyro-process and a fluoride-volatility process.

Process steps that were examined and eliminated include (1) laser perforation of the cladding, (2) chemical or electrochemical dissolution of the cladding, (3) dissolution of the fuel in hydrochloric acid, and (4) the use of inorganic ion-exchangers for separations (based on lack of available materials).

2.2 FLOWSHEET OPTIONS

The favored process steps can be assembled into five general options (Fig. 1). The LTR case, which can be assured of operation and requires a minimum of additional development, is shown as Option I. This option results in two possible products: (1) a low-activity metallic plutonium product for IFR fuel and a highly radioactive actinide-lanthanide oxide product which would be sent to the on-site recycle plant (a new process may be necessary at the IFR plant for conversion of oxides to metals or chlorides), or (2) a single product of contaminated plutonium produced by blending the streams of the first product option which would be converted to fuel for the IFR. The second and third options yield a mixed transuranium-fission product oxide product (minus uranium) that would be fed to the

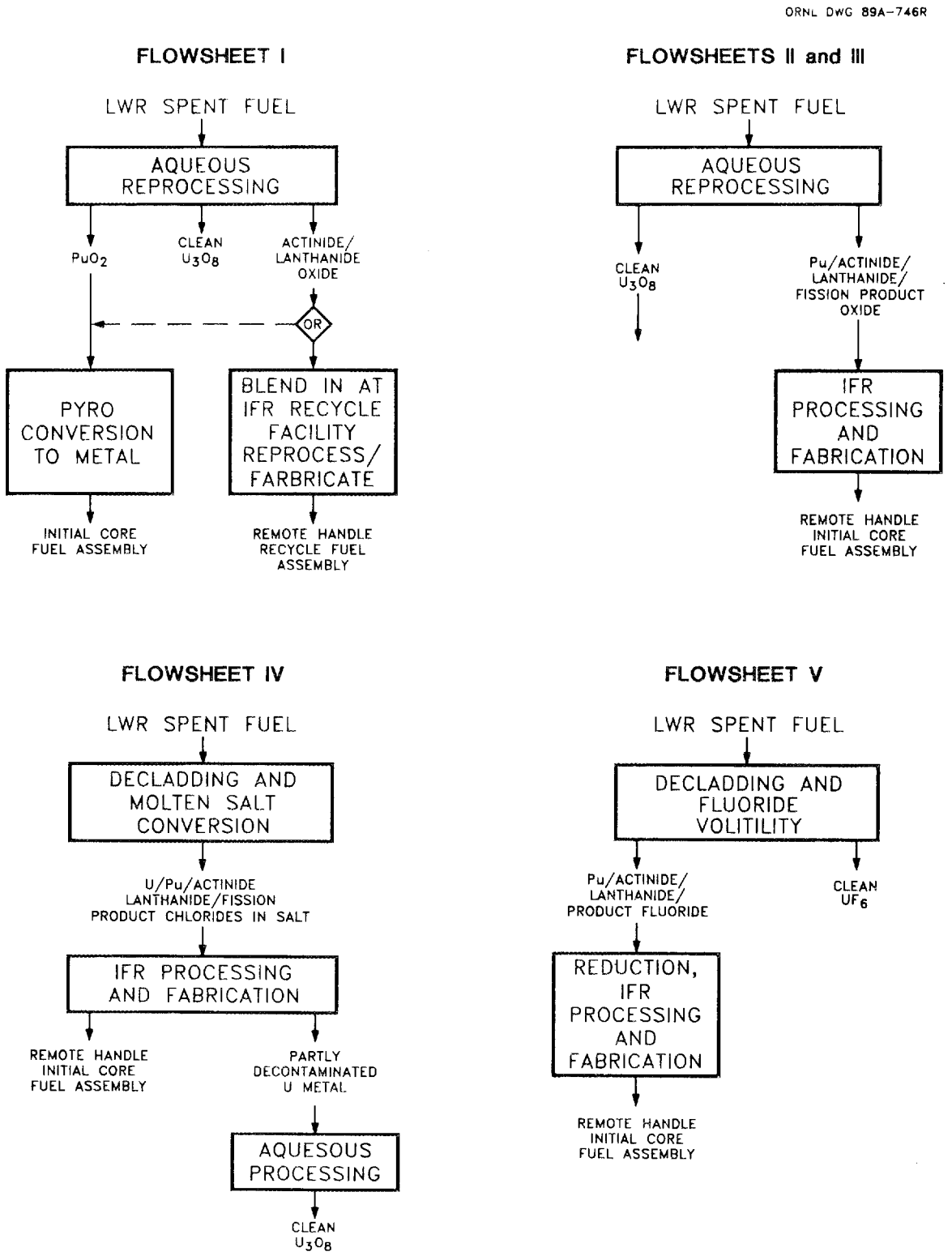

Fig. 1. Basic LWR spent fuel reprocessing options to yield LWR fuel.

on-site IFR plant (a new process step may be required at the IFR plant for conversion of oxide to metal or chloride). These options deviate sufficiently from current technology that more development work would be required. Option IV uses pyro-processing; this flowsheet would require significantly more development than the other options. Option V uses fluoride volatility methods and would yield a fluoride product which would be reduced to metal.

2.3 CONCEPTUAL FLOWSHEETS

Several flowsheet approaches to the general problem of recovering actinides from LWR fuel and converting them to a form suitable for IFR fuel were considered. The five flowsheets shown here (Fig. 1) include a number of options for the different process steps, and a very large number of combinations can be devised. These flowsheets are presented not as specific recommendations, but they are intended to provide a basis for considering options and estimating the scope of development work that will be required.

The flowsheets with the least uncertainty are based on adapting the basic PUREX process for uranium/plutonium recovery, adding TRUEX for recovering the minor actinides, and then using known or reasonably well-understood processes for the initial conversion steps for the products. Three of the conceptual flowsheets are based on aqueous chemistry. These are (1) the LTR PUREX-based Flowsheet, (2) a Low-DF PUREX-based Flowsheet, and (3) a Direct Precipitation Flowsheet. Many variations of these flowsheets are possible. The interfaces with fuel fabrication have not been fully examined and specified, so several possible options are given.

Since the process necessarily includes a conversion from an oxide fuel to a metal fuel there must be a cross-over from the oxide to the metal system. Some of the steps involve pyrochemical processes related to the IFR fuel recycle process, and it is assumed that full development and demonstration of that process will be done outside the scope of this study. Others involve an extension of the IFR process to include oxides, and these processes are less well defined. Current work in the Atomic Vapor Laser Isotope Separation (AVLIS) and Special Isotope Separations (SIS) programs in developing methods for uranium and plutonium metal production and existing technology used for plutonium metal production, can provide a background for the oxide-to-metal conversion process. It is expected that significant additional development would be required.

Two dry processes are proposed, one based on pyroprocessing and related to the IFR blanket process, and the other based on work done prior to 1970 at ANL and ORNL on fluoride volatility. The pyroprocess flowsheet is not defined sufficiently to completely specify the process steps, but it consists of decladding the fuel by volatilizing the zirconium as $ZrCl_4$ and then dissolving the fuel in a molten chloride salt for processing with an IFR type flowsheet. The fluoride volatility process is

based on the removal of uranium as UF_6, leaving nearly all other LWR fuel constituents combined as a residue.

2.3.1 LTR PUREX-Based Process (Flowsheet 1)

This process (Fig. 2) is based on producing separate decontaminated uranium and plutonium products and a fraction containing trivalent actinides (americium and curium) and rare earths. Neptunium can be put into one of these products or withdrawn separately, depending on valence control; we assumed it was combined with the plutonium product and ended up in the IFR fuel. The uranium product is decontaminated for storage or recycle to enrichment. The plutonium product (probably also containing neptunium) would be converted to PuO_2 and finally to metal for fabrication of the alloy fuel. Current methods use calcium reduction in small batches; but a pyrometallurgical process would be preferred, either at the reprocessing site or at the IFR site, using the IFR fuel recycle equipment. The plutonium product and the fraction containing trivalent actinides and rare earths, can, if desired, be recombined prior to production of the IFR fuel.

We anticipate that reactor startup would be simplified if the fuel was fabricated at the reprocessing site, since that would allow a delay of several years before the fuel recycle equipment at the reactor needed to be operated. In addition, it would probably be advantageous if the initial fuel was not unnecessarily radioactive. Therefore, the actinides (other than plutonium and neptunium) and any associated fission products could be (a) stored temporarily until the IFR recycle plant is running and then blended into recycle fuel, (b) blended into the initial metal fuel alloy at reactor startup, or (c) fabricated into separate irradiation targets, independent of fuel. Since the actinides can be separated into fractions, some of them that might have particular value (such as neptunium for producing ^{238}Pu) could be withdrawn from the fuel cycle and irradiated separately for such special purposes. Comments regarding the major process steps (shown schematically in Fig. 2) follow.

2.3.1.1 Mechanical Operations

The mechanical operations could include disassembly and removal of hardware such as end fittings, so that only fuel assemblies would be processed. These operations would decrease the amount of TRU waste somewhat, but would be at the expense of equipment complexity. They would include shearing of the fuel assemblies. Other options are available; but they are not developed and proved, as is shearing.

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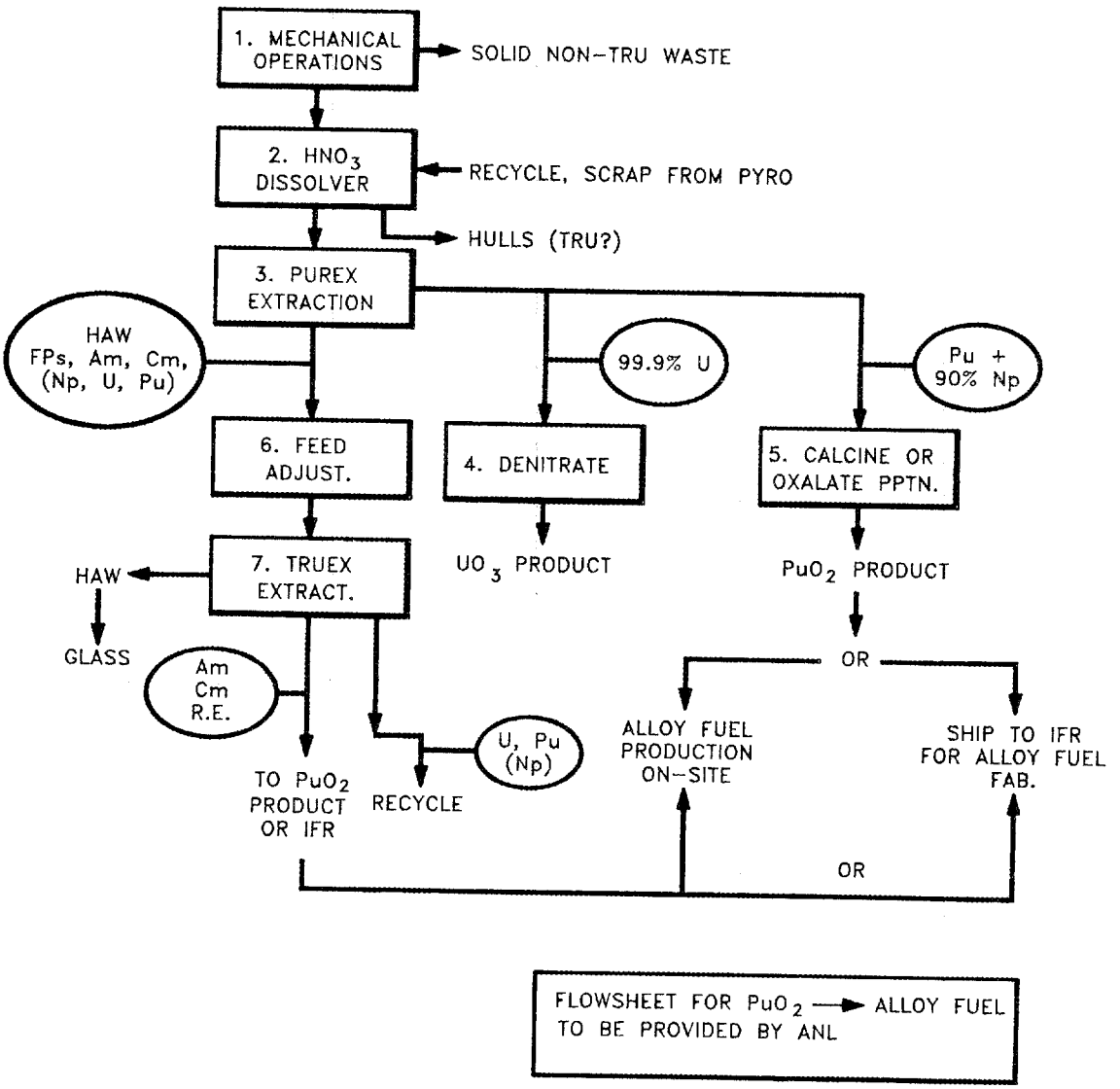

Fig. 2. LTR PUREX-based process (Flowsheet I).

2.3.1.2 Nitric Acid Dissolution

Nitric acid dissolution of LWR fuel is a well-demonstrated operation, the main problem is to decide on the particular type of dissolver to use. There would also be a need for equipment to handle recycle streams (mainly tanks and evaporators) and to deal with scrap returned from the pyroprocess for making metal fuel, whatever flowsheet is used. Scrap recycle, which would include mechanical equipment and dissolvers or leaching systems, has become a major operation in plants that handle plutonium metal.

2.3.1.3 PUREX Extraction

The PUREX process is used in all reprocessing plants in several countries. One of several standard PUREX flowsheets would be used, yielding (1) decontaminated uranium and plutonium products, (2) a high-level aqueous waste (HAW), and (3) possibly a medium- or low-level aqueous waste. At least two decontamination cycles would probably be used to produce decontaminated uranium and plutonium products. It is probably advantageous to select conditions such that as much as possible of the neptunium (probably >95%) will go to the plutonium product. However, if a separate neptunium product is desired, it could be routed with the HAW for recovery (Fig. 2) in step 7. Neptunium management is the main difference between this flowsheet and existing processes. Technetium management must also be considered with respect to both uranium product specifications and long-term hazard in the waste.

2.3.1.4 Denitrate

The uranium product would be denitrated or calcined and converted to the oxide which would then be sent to conversion and, for storage or recycle to enrichment. There are demonstrated plant-scale processes for this step.

2.3.1.5 Oxide Conversion

The plutonium product (probably but not necessarily containing 95% of the neptunium) would be converted to oxide. There are demonstrated processes for this conversion, including direct calcination or precipitation with oxalic acid followed by calcination.

The plutonium oxide product would be converted to the metal, adjusted to the proper alloy composition, and formed into fuel assemblies. There are several potential processes for this procedure. Current technology for plutonium metal production uses conversion to fluoride followed by metal (calcium) reduction in small batches, and there is ongoing work to develop improved processes (direct oxide reduction). In addition, the AVLIS program is developing conversion

processes to produce uranium metal which may be applicable to this problem. Further evaluation is clearly needed.

We assumed that the conversion would be carried out on-site in a process based on development work from ANL or the AVLIS program, and the metal fuel fabrication would use a process based on the IFR fuel recycle process. In this latter case, the final product would be fuel assemblies for the first core load of the IFR. As an option, the actinide oxides could be shipped to the IFR site and converted to fuel assemblies in the IFR recycle equipment (an additional process step may be needed at the IFR to convert oxide to metal or chloride). We anticipated that shipment of IFR fuel could be accomplished more readily than shipment of the oxides. In either case, the oxide or fuel (whichever is the product) could be highly decontaminated, or various actinide and fission product fractions (from step #7) could be added to it.

The HAW from the first extraction cycle will contain nearly all the fission products, americium, curium, part of the neptunium (from 5 to 90%, depending on conditions), and residual uranium and plutonium (probably of the order of 0.1%). Various other aqueous wastes will likely be concentrated by evaporation and added to the HAW, and the combined waste will be feed adjusted (if necessary) for an actinide recovery process. The goal is to reduce the actinide content of the HAW to meet the desired levels to be defined for the waste.

2.3.1.6 Feed Adjustment

Possible processes for actinide recovery from the HAW include TRUEX (shown here) and cation exchange. Feed adjustment for either one will involve valence adjustment (probably strong reduction) to convert neptunium to an extractable species, and probably addition of a complexing agent (such as oxalic acid) to reduce interference from metals such as Zr and Fe.

2.3.1.7 TRUEX Extraction

The TRUEX process has been demonstrated in countercurrent processes with various plutonium recycle materials, but not with HAW containing the full range of elements. As usually applied, americium, curium, and rare earths are collected as a trivalent element product, plutonium as a second product, and uranium as a third. It is likely that plutonium could be routed with the trivalent fraction. The uranium, neptunium, and plutonium can readily be recycled within the plant. The trivalent product would be sent to the IFR for transmutation, either immediately or after interim storage. It could be either blended with the plutonium alloy fuel or fabricated into separate irradiation targets. The behavior of neptunium can be controlled by valence adjustment and other flowsheet parameters. Clearly, some further development of TRUEX is needed, especially for neptunium; and a better definition of the goals of the process must be developed.

If separation of rare earths from trivalent actinides is required, a considerable development effort may be necessary. For this study, we assumed that the actinides and rare earths can be introduced into the IFR pyroprocesses during IFR recycle, and any necessary separation will be accomplished there. Conventional aqueous methods use concentrated LiCl solutions versus anion exchange resin or amine extraction, but those are not appropriate for this system. There is French data indicating an amide extraction process might be satisfactory, and some other unusual extractants have been proposed. There is current work in a different program on the separation of americium (but not curium) from rare earths by valence adjustment, but a process has not been demonstrated. The separation requirements need to be better defined, and then possible flowsheets can be proposed.

2.3.2 Low-DF PUREX-Based Process (Flowsheet II)

This process (Fig. 3) is somewhat similar to Flowsheet I except that plutonium is never separated from most of the radioactivity. The products are clean uranium for storage or recycle to enrichment and a highly radioactive plutonium containing americium, curium, neptunium, rare earths, and some other fission products. The following steps are shown schematically in Fig. 3:

1. Mechanical operations are the same as for Flowsheet I.

2. Dissolution, recycle, etc. are the same as for Flowsheet I.

3. Feed adjustment includes a chemical reduction to convert plutonium to the +3 valence, which we expect to also convert neptunium to the +4 valence state.

4. The TBP extraction step removes and decontaminates uranium and most of the neptunium. This might be done in the first cycle or the second cycle, as in the proposed ORNL-HEF and Exxon flowsheets (both not demonstrated). Plutonium, americium, curium, fission products, and part of the neptunium remain in the aqueous phase.

5. The uranium + neptunium stream is treated to adjust neptunium to the +5 valence state.

6. The second TBP cycle is used to decontaminate uranium further and to remove neptunium into the aqueous extraction raffinate, which is combined with the raffinate from step #4. Alternatively, a pure neptunium product could be withdrawn.

7. The clean uranium product is denitrated and treated as in Flowsheet I, step #4.

8-10. The combined aqueous raffinates from steps #4 and #6 contain all the plutonium, neptunium, americium, curium, and fission products. Several options are available to convert these to an oxide product. One is oxalate precipitation (#8) to precipitate nearly all the plutonium, neptunium, americium, curium, rare earths, and some other fission products as oxalates, which are then calcined to oxides (step #9). Residual actinide metals left in the supernate would be recovered by TRUEX extraction or cation exchange and recycled back to step 2. An alternative (Step #10) is to use direct calcination or a process analogous to the COPRECAL[1] process used for producing LWR fuel. The COPRECAL

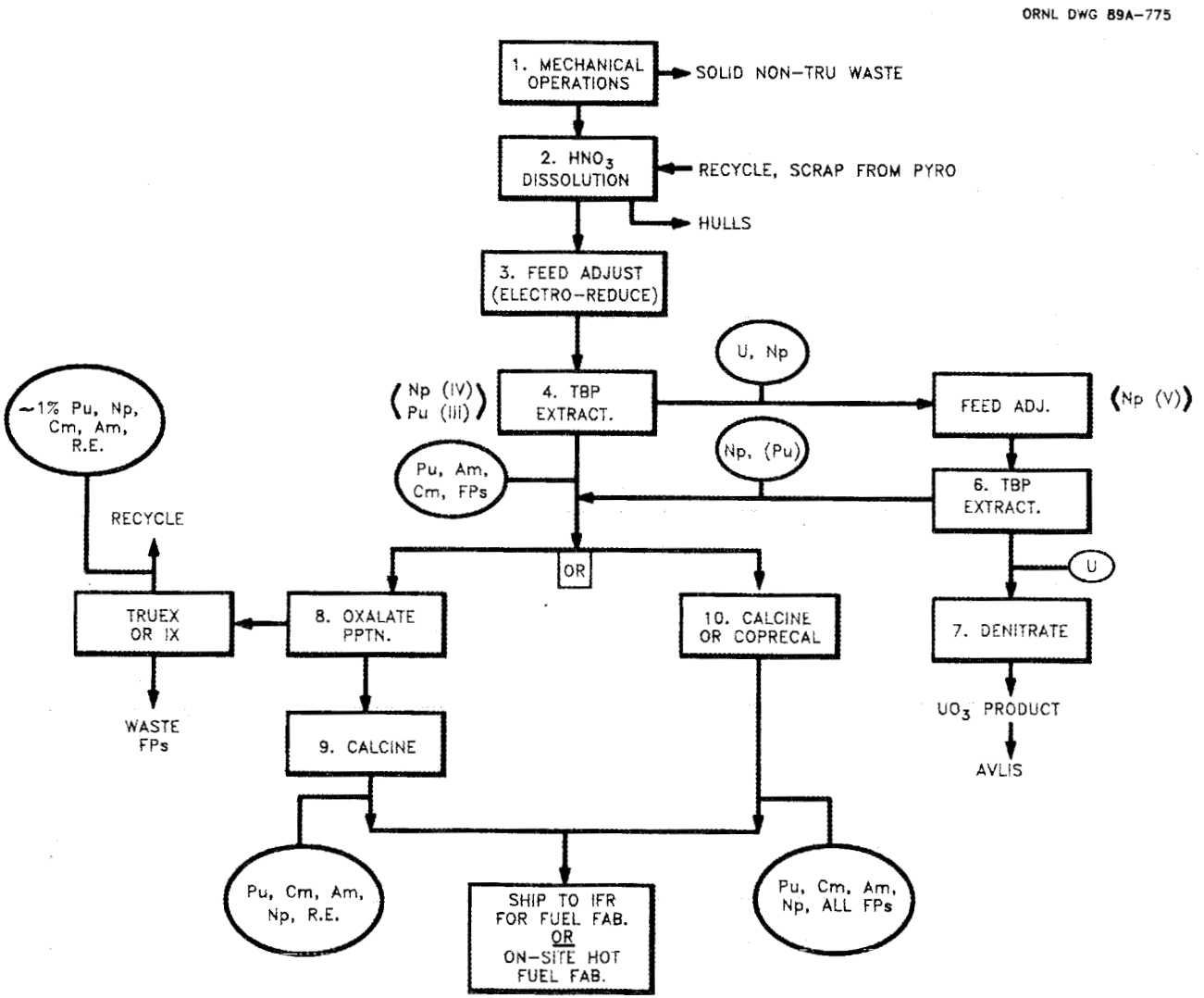

Fig. 3. Low DF PUREX-based process (Flowsheet II).

process involves the coprecipitation of a nitric acid solution of uranium and plutonium with ammonium hydroxide and subsequent calcination, in a fluidized bed, to the mixed oxide powder.

The plutonium oxide product (from step #9 or #10) would be converted to the metal alloy fuel as described for step (5) of IFR Processing Scheme I.[2] The major difference for this flowsheet is that the conversion to metal and finally to fuel assemblies necessarily takes place with an extremely radioactive feed and the plutonium product is never decontaminated to a substantial extent, so the plutonium must always be handled and shipped as a very high-level radioactive material. This method has safeguards advantages, but would complicate the fuel cycle.

Also, since plutonium is never separated from the actinides other than uranium, the options of separating actinides into individual fractions or generating a pure plutonium product free of other actinides (which might be advantageous for IFR startup) are less available.

2.3.3 Direct Precipitation Process (Flowsheet III)

This concept (Fig. 4) is based on (1) direct precipitation of a plutonium product containing most of the actinides, rare earths and some other fission products, (2) subsequent PUREX recovery of uranium from the supernate, and (3) a scavenging process to recover and recycle residual actinides from that aqueous raffinate. This procedure necessarily yields a highly contaminated plutonium product and does not allow for separation and alternative management schemes for any of the actinides.

2.3.3.1-2 Mechanical Operation and Nitric Acid Dissolution

These steps are essentially the same as for Flowsheet II.

2.3.3.3 Oxalate Precipitation

The oxalate precipitation would be done on a diluted feed stream at high temperature so that most of the uranium would remain in the supernate. It may turn out that uranium must be removed before this step, in which case this flowsheet more closely resembles Flowsheet II.

2.3.3.4-5 Filtration and Calcination

The oxalate precipitate would be collected, washed, and calcined to produce the plutonium oxide product containing also americium, curium, neptunium, rare earths, and some other fission products. It would be handled as in IFR Processing Scheme II.

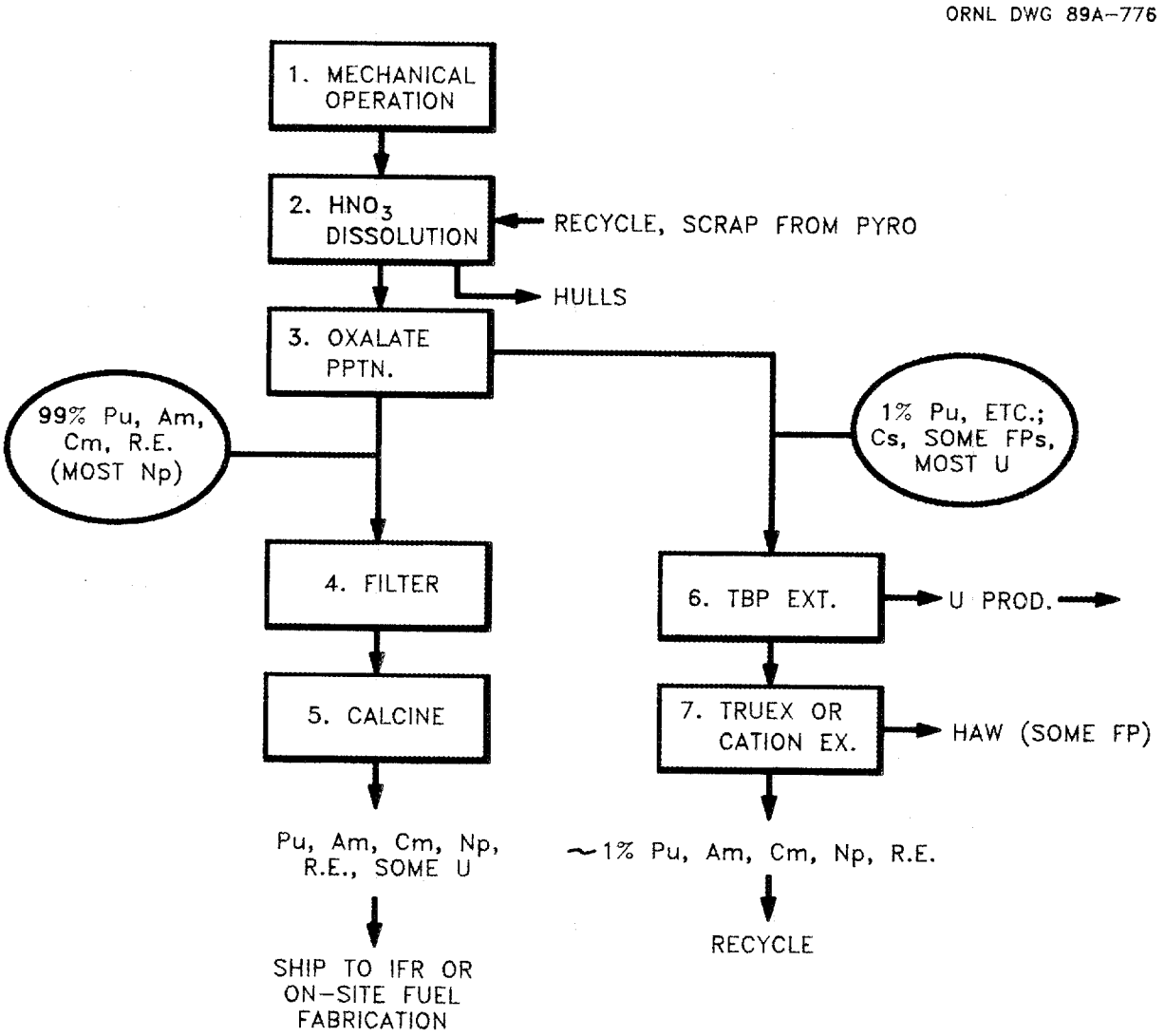

Fig. 4. Direct precipitation process (Flowsheet III).

2.3.3.6 TBP Extraction

Uranium would be recovered by TBP extraction from the supernate, perhaps after prior concentration by evaporation. Two cycles would probably be required to decontaminate the uranium product adequately for enrichment. The residual uranium, plutonium, americium, curium, neptunium, etc., in the raffinates would be recovered by a TRUEX cycle or cation exchange, as in the other flowsheets, and this material would be recycled to step #2. The comments given for Flowsheet II regarding metal production would generally apply to this product, also.

Note that, although this process may appear simpler, it requires about as much equipment and space as the others because headend and PUREX processing to decontaminate the uranium really dominate the overall plant. It is almost immaterial, in this respect, whether the plutonium is decontaminated or not. However, if the plutonium is not decontaminated, the oxide-to-metal conversion and fuel element fabrication will be considerably more difficult.

2.3.4 Non-Aqueous Pyroprocess (Flowsheet IV)

Since the final product is metal (Fig. 5), it is necessary to use nonaqueous pyrochemical processes at some point in the flowsheet. This suggests that an advantage might be realized if nonaqueous processes are used throughout. This flowsheet is an attempt to sketch out what such a flowsheet might look like. It is not clear that any of the steps would actually accomplish their intended purpose, and we propose this scheme only to focus consideration and to gain input from others.

2.3.4.1 Mechanical Operation

There would be disassembly to remove hardware components (especially iron alloys) from the LWR fuel. It is probably necessary to break fuel assemblies into shorter segments, but shearing to a few inches might not be required.

2.3.4.2 Chlorination

Chlorine gas should react with the Zircaloy cladding at a relatively low temperature to produce volatile $ZrCl_4$, and it should not react with the UO_2 fuel. This could be done dry or, possibly, in a molten chloride salt. An alternative would be dissolution of the cladding in a liquid metal. Experimental demonstration of decladding would be required.

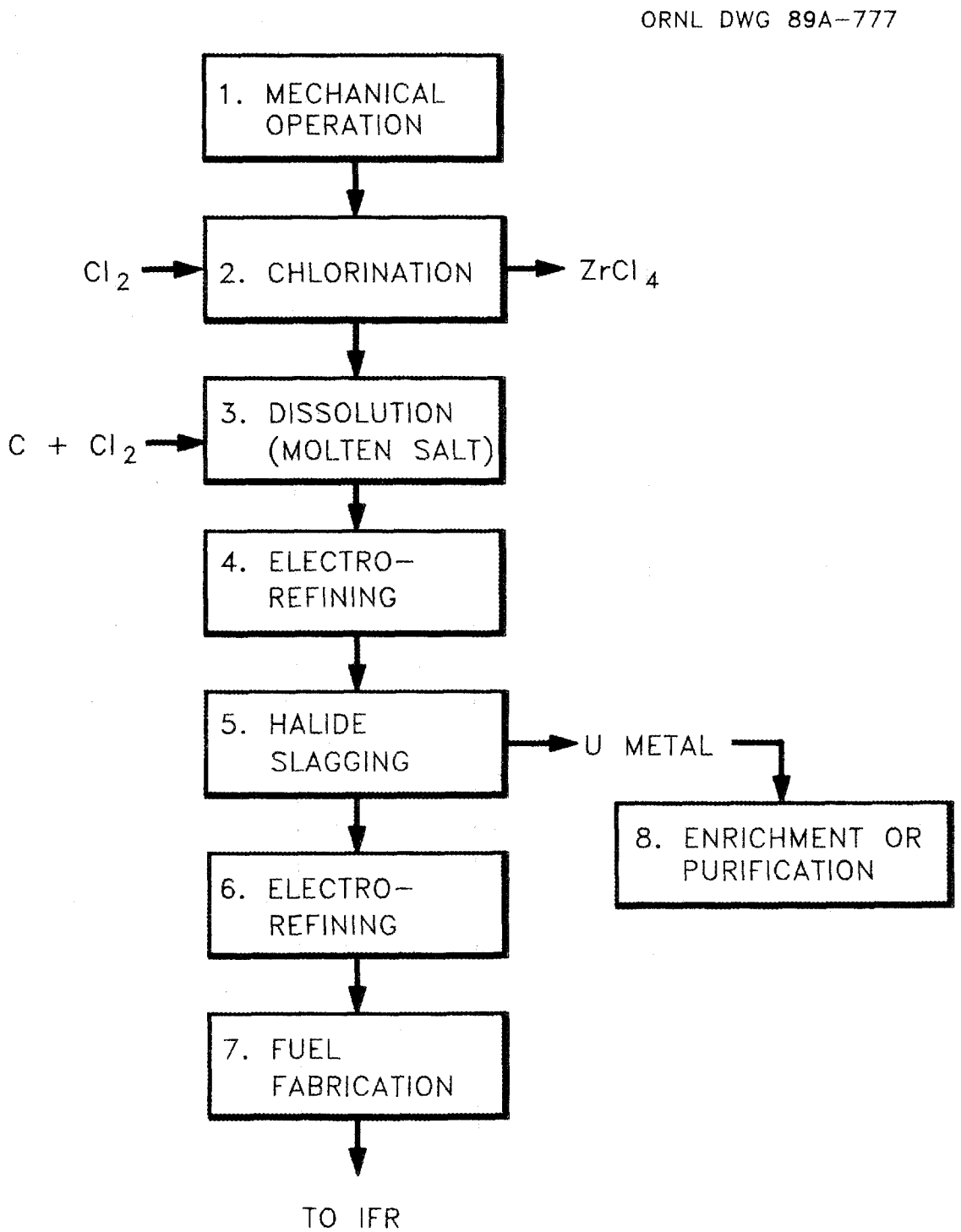

Fig. 5. Nonaqueous process (Flowsheet IV).

2.3.4.3 Dissolution (Molten Salt)

The oxide fuel would then be dissolved in a molten chloride salt using $COCl_2$ or carbon and chlorine, giving the chlorides of uranium, plutonium, other actinides, and fission products. The dense UO_2 fuel may be rather nonreactive, so demonstration would be required.

2.3.4.4-6 Electrorefining

This salt would then be treated by electrorefining and halide slagging to remove most of the fission products, convert the actinides to metals, and separate part of the uranium to produce a plutonium product suitable for IFR fuel production. This process would be similar to that proposed for recycle of the IFR blanket.

2.3.4.7 Fuel Fabrication

The plutonium metal would be mixed with alloying elements and cast into IFR fuel assemblies.

2.3.4.8 Enrichment or Purification

It is not clear what should be done with the excess uranium. It might be converted to an alloy appropriate for AVLIS feed, but any enrichment process would require a greater measure of decontamination from fission products, other actinides, and impurities. If it is stored as a waste, the cost would be large, unless it was further decontaminated. It is possible that an aqueous process, such as PUREX, would be required to decontaminate the uranium in any case.

One potential problem with this approach (and also with the IFR recycle process) is that a small fraction of the americium and curium may not follow the plutonium product but would remain in the salt phase instead. If a fraction of the americium and curium did follow the salt phase, it would have to be recovered for the partitioning concept to be successful. It could be recovered by pyrohydrolysis with steam, dissolution (almost certainly in an aqueous chloride system), and a variation of the TRUEX process; but that would defeat most of the advantage of the nonaqueous approach. The same reasoning also suggests that a small fraction of the actinides from the IFR normal recycle operation may have to be separately recovered. This point has not been included in any of the flowsheets, except in the broad context of recycle from IFR. The situation, with respect to waste losses in the nonaqueous processes, requires much better definition.

2.3.5 Non-Aqueous Fluoride Volatility Process (Flowsheet V)

A limiting situation is to remove only cladding and >90% of the uranium from LWR fuel (Fig. 6) and send everything else to the IFR fuel fabrication. This goal can be approached by combining a headend decladding operation with a halide volatility process, of which fluoride volatility is best known. Extensive studies were carried out starting about 40 years ago. Such a flowsheet could consist conceptually of the following steps:

2.3.5.1 Mechanical Operation

Mechanical headend to remove as much hardware and non-fuel-containing material as possible. This is especially important in volatility processes.

2.3.5.2 Decladding

Decladding to remove the large amount of Zircaloy from the oxide fuel, because only a small fraction of the zirconium can be tolerated in either the uranium or plutonium products. It is possible that zirconium could be separated from the products later, but there would still be excessive amounts of tin and other metals that would cause problems. Several decladding processes might be possible, including the following:

A. Voloxidation to convert the oxide fuel to powder that could be physically separated from the cladding. This process has been demonstrated, but there is a question as to the extent of loss of fuel with the cladding waste. One might hope that this could be much less than 1%. This is the process shown on the flowsheet (Fig. 6, step 2).

B. Oxidation, or formation of a combined oxide-nitride of the cladding by reaction with air, at a higher temperature than voloxidation. This would form a fragmented or powdered zirconium oxide or oxynitride that is much less dense than the uranium oxide fuel,
so it could be separated by some physical means such as flotation with a liquid metal or alloy, perhaps based on cadmium which is used in the IFR process anyway.

C. Reaction with chlorine, Hcl, or possibly another halide (but not fluoride) to convert the cladding to volatile $ZrCl_4$ without affecting the oxide fuel. This might leave excessive amounts of impurities that do not form volatile chlorides.

D. Dissolution of the Zircaloy in a liquid molten salt or metal alloy that does not attack the oxide fuel. There are several more or less unlikely possibilities for this method.

2.3.5.3 Fluorination

Conversion of the oxide fuel to a chemical form from which uranium is volatile but plutonium, other actinides, and most fission products are not substantially volatile. This might be accomplished with other halides, especially the chloride; but the fluoride route appears most suitable; and that approach

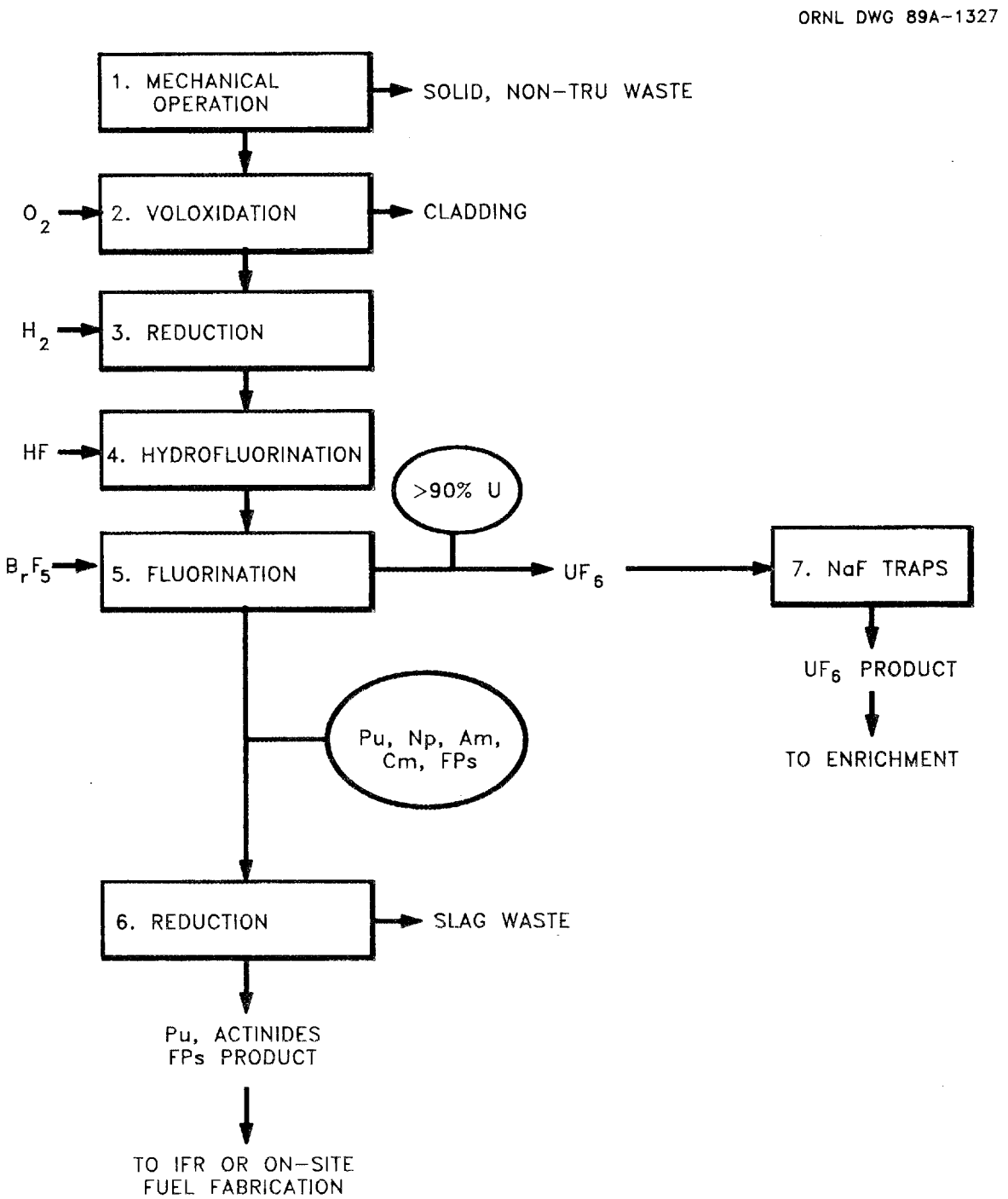

Fig. 6. Nonaqueous fluoride volatility process (Flowsheet V).

will be followed through the rest of the flowsheet discussion. However, we believe it is worth examining the chloride route.

As the fluoride conversion process is normally carried out, the oxide fuel, if oxidized by voloxidation, would first be treated with hydrogen to reduce it to the tetravalent uranium state. The oxides (predominantly UO_2) would be hydrofluorinated with HF to produce UF_4 and appropriate fluorides of plutonium, other actinides, and fission products. This process is done industrially in the uranium industry, even with rather impure uranium oxide, and has been demonstrated with irradiated fuel.

The dry fluorides would be fluorinated under strongly oxidizing conditions with compounds such as interhalogen fluorides (BrF_5, ClF_3, BrF_3). These reactions will produce UF_6 gas (along with small amounts of very few volatile fission product fluorides) and leave nearly everything else in the form of non-volatile or at least less volatile compounds. Considerable work has been done on similar processes prior to 1970. Elemental fluorine could be used, but in that case neptunium and plutonium might be more volatile (see below).

2.3.5.4 Reduction to Metal

The residue, containing the plutonium, neptunium, trivalent actinides, nearly all fission products, probably some cladding fragments, a small fraction (up to a few percent) of the uranium, and various impurities, mostly as fluorides but some possibly as metals or oxyfluorides, can be converted to metal for feed to the IFR process. An oxide-to-metal conversion process would be necessary, which would be based on existing technology to the extent possible. Testing of known methods and additional development would be required.

2.3.5.5 Fluorination and Sodium Fluoride Trapping

It is possible to volatilize PuF_6 by oxidation with elemental fluorine or the very reactive compound O_2F_2 (or FOOF). However, these reactions are difficult, generally requiring a fluidized bed and complex procedure. In view of the presence of larger amounts of other elements, it is reasonably likely that fluidized bed operation would be an engineering impossibility. In any case, these highly reactive fluorinating agents are handled differently than the interhalogens. With this feed material, the recovery by fluoride volatility of a significant fraction of the plutonium as a clean product is probably not practical; and it certainly would not be easy.

It appears to be very difficult to modify this process to produce a purified plutonium product. Although plutonium can be volatilized as a fluoride under carefully controlled conditions, it is a difficult reaction to accomplish, yields tend to be low, and in any case, it would still be substantially contaminated with some fission products.

The UF_6 can be further decontaminated by fractional distillation or by absorption/desorption on NaF traps, passing it through heated NaF traps, or both. The fluorides of a few elements are sufficiently volatile that their separation from uranium fluoride can cause some problems,
notably these elements are neptunium, ruthenium, technetium, tellurium, and molybdenum. The NaF absorption process provides reasonably good uranium decontamination and also offers a possible way to recover a separate neptunium fraction. Thus, UF_6 could probably be decontaminated adequately for direct feed to an enrichment plant using UF_6 or for storage; alternatively, the uranium could be reduced to the metal for feed to AVLIS. All these operations have been demonstrated under a variety of conditions, some of them on an industrial scale.

Initially, this flowsheet appears to be attractive. Many of the individual process steps have been demonstrated, and some are used in the uranium industry on an industrial scale, but only in the absence of high radiation levels. Several individual steps were tested about 40 years ago in small-scale experiments with irradiated metal (at ANL) and in the late 1960,s with oxide fuels (at ANL and ORNL). However, the remote maintenance of this sort of equipment under plant conditions with irradiated fuels appears to present some very formidable problems. At the very least, a substantial development program would be required; and at worst, the practical operability of the approach is in question.

2.3.6 Technological Bases of the Flowsheets

We shall define three levels of technological bases for possible flowsheets in this Section. In turn, these levels will relate directly to the amount of development work that would be required to provide confidence that such a flowsheet would be operable. They will also be used to establish its performance, or to define modifications that would be necessary for it to be practical. We strongly feel that only a flowsheet based on demonstrated technology could be successfully built and operated in the near future with a reasonably firm cost basis and schedule. Any other option would require a significant development program leading to uncertainties (schedule, costs, and operability). We believe it is entirely possible that some of the proposed flowsheets contain parts that are fundamentally impractical.

1. Demonstrated technology includes an integration of flowsheets and processes that have been documented and operated successfully with truly realistic feed materials to produce the stated products on an industrial scale over an extended period of time in independent facilities located at more than one site.

2. Projected technology includes flowsheets and processes that are based on significant experimental laboratory or engineering demonstrations that fall short of meeting all the requirements for demonstrated technology in some significant way (such as non-realistic feed material or other operating conditions, small-scale or short-term operation, system integration deficiencies, or inadequate verification).

3. Hypothetical technology includes flowsheets and processes based on limited small-scale laboratory experiments and theoretical calculations, but lacks an engineering demonstration under realistic process conditions to a substantial extent.

On the basis of these definitions, we suggest the following categorization of the five flowsheets given in Fig. 1. Flowsheet I, involving standard PUREX, is largely demonstrated technology, although the TRUEX section might be considered projected technology. Flowsheet II is a combination of demonstrated and projected technology. Flowsheet III includes substantial elements of hypothetical technology, and Flowsheet IV is largely hypothetical technology. Flowsheet V is a combination of projected and hypothetical technology. All manipulations of neptunium that divert it quantitatively into one stream involve some degree of projected technology.

2.4 PRODUCT FORM OPTIONS

In this initial study, the choice of products from the LWR recovery plant was briefly examined and possible options identified. For the fissile/actinide product, two characteristics need examination: (1) the chemical form of the product, and (2) the degree of purification of the products from fission products. The plutonium product could be oxide, metal, or chloride. The uranium product must be decontaminated from all fission products and actinides, and be in an oxide or metallic form, if it is to be recycled for enrichment or to avoid being classified as a transuranic waste with the associated, high, waste storage costs.

Factors which also must be taken into account include: (a) transportation requirements, (b) chemical processing options and appropriate interfaces with the LMR recycle facility, (c) economic and fuel cycle optimization considerations, and (d) waste management considerations in lieu of uranium enrichment. The first two items are discussed briefly below. Some observations on the third are included in Section 3.

2.4.1 Transportation Requirements

The special requirements for shipping plutonium (10 CFR 71.63) including, double packaging, criticality safety, etc., limit how it may be shipped. Although a soluble form is not now specifically prohibited, nitrate or chloride products are not desirable in order to mitigate risks in accidents and may be restricted in future regulations. These considerations make it desirable to have a metallic or

consolidated oxide form for the shippable product. The regulations specifically recognize that a fabricated fuel assembly provides a high integrity package. The fuel assembly meets several of the requirements which impose additional packaging operations for plutonium in other forms. Shipment of the product of the LWR facility as fuel assemblies simplifies meeting requirements and assures meeting transportation regulations. Shielding requirements for the materials will depend on the degree of decontamination of the various products from high-energy beta-gamma and/or neutron radioactive species.

2.4.2 Chemical Processing Options and Appropriate Interfaces with LMF Recycle Facility

This brief evaluation did not attempt to determine optimal strategies for integrating the LWR reprocessing and conversion steps with the advanced LMR fuel cycle. However, based on the requirements for transportation, it appears that the preferred product from the LWR recovery facility will be a consolidated oxide or metallic form, perhaps even a completed fuel assembly.

Observations relevant to determining the distribution of actinide components in the product include:

1. For several reasons, it may be desirable to include the recovered neptunium with the plutonium product. Neptunium and plutonium have similar behavior in fast reactors (both fission), similar criticality issues, and similar handling characteristics. However, an alternative option is to produce a separate neptunium product.

2. The other actinides could either be included with the plutonium or shipped separately, depending on a number of interacting factors.

3. The dominant fission products by weight are the lanthanides, which are difficult to separate from the minor actinide fraction by aqueous processes. There is an incentive to remove these lanthanides at the reprocessing plant to avoid shipment of a highly radioactive material to an IFR facility at the power plant and then reshipment to a disposal site. If fuel assemblies were manufactured at the LWR reprocessing plant, partial separation of the lanthanides from the actinides would be desired prior to fuel fabrication. This separation could either be by some aqueous process or by a pyro-process, and this step would require development. The ANL pyro-process is capable of partial separation of actinides and lanthanides giving the option of shipping these materials together to the LMR recycle plant or using the IFR process at the LWR reprocessing plant.

Considering the above factors, the following product options were identified. These should be further assessed in future systems studies:

1. Two products: (1) completed fuel assemblies containing decontaminated plutonium and the major portion of the neptunium (if desired), and (2) a minor actinide/lanthanide oxide or metal product to be further treated and incorporated into LMR fuel after initial startup of the LMR recycle plant.

2. Fuel elements containing all the actinides after partial separation of the lanthanides.

3. Two products: (1) a fissile fraction (oxide or metal) to be converted to fuel at the LMR recycle plant prior to startup of the reactor, and (2) a minor actinide/lanthanide oxide or metal product as in the first case.

4. An actinide/fission product oxide or metal product containing some portions of the lanthanides and other fission products, to be treated and converted to metal and fuel at the LMR recycle plant.

From the analyses in this study, options 1 and 2 appear to be the preferred choices.

3. PRELIMINARY PERSPECTIVE ON ACTINIDE RECOVERY COSTS AND FUEL CYCLE OPTIMIZATION

In this initial study, we did not attempt a cost analysis. Based on earlier estimates of costs for PUREX plants and variations required for Actinide Partitioning-Transmutation,[3] it appears that there will be a modest cost increase for actinide and fission product recovery. This cost will be relatively small and it will be partially off-set by savings in fuel requirements and in waste management over the long term.

Because of the similarities between the LTR case and the similar processes in the Actinide Partitioning-Transmutation studies of a decade ago,[3] some perspective on costs exists. The separate reprocessing waste treatment facility, in which the actinide recovery was done, was estimated to cost 42% as much as the reprocessing plant itself. Note, however, that the estimated increased cost resulted from inclusion of many additional treatment steps for waste streams. The extra costs due to this element in the overall system added some 7% to the total fuel cycle costs over that of the reference system, which utilized conventional reprocessing. The overall electric power costs in that study were 5% higher for the actinide burning case. Because of the many differences between the present starting case of a throw-away fuel cycle and that of the earlier study, as well as the differences because the general scenario envisioned today uses metal-fueled LMRs, the earlier costs can only indicate some aspects of the cost framework.

We can make two observations relative to the present conditions. First, by integrating actinide recovery and waste treatment with the reprocessing plant, some savings should be possible. In support of this, some recent estimates made at Hanford of differential costs associated with TRUEX processing of PUREX wastes, have indicated these costs alone could be significantly less than the 42% increase mentioned above. However, the earlier study also included costs for treating various sludges, filters, etc. resulting from the total process operations. When all flowsheet modifications and facilities are efficiently integrated, significant cost savings may be possible compared with earlier studies. The savings could also be increased for more modest recoveries of the minor actinides. Until all necessary peripheral steps in processing and waste treatment have been considered and more detailed studies

made of the potential for cost reductions, an estimate of 25% for the net cost increase for minor actinides recovery is recommended as an upper boundary. This translates to an increase of about 3% in power generating costs.

Secondly, neither here nor in the earlier study, was any attempt made to examine the cost differentials due to the introduction and deployment of the LMRs. In addition, potential cost savings exist because of simplification of the repositories as well as the long-term, but difficult to analyze, value of capping the price of uranium.

If the perspective described here is within reason, one can conclude that actinide burning, in isolation, will probably add some small increment to the fuel cycle costs and, at most, ≤5% to power costs. Considerable additional study and analysis are required to understand and refine these cost estimates. In all likelihood, other factors related to reactor and repository costs will have an impact at least as large as the fuel cycle cost increment.

In Section 2.4 on product forms, some "chemistry" considerations in choosing the product form were described. In addition, a more thorough assessment needs to be made of possible cost savings or other criteria for optimizing fuel cycle configurations from a "total systems viewpoint." For example, some economic penalties might be incurred if all plutonium fuel fabrication capabilities were restricted to the fuel cycle facilities co-located with the LMRs. This comes about for two reasons. First, since the initial core fuel requirements (for the PRISM ALMR design) are 4 to 5 times the average annual requirements, the co-located fuel facility would have to be started about five years prior to reactor power operation, in order to fabricate the initial core fuel (if there were no increase in the fabrication capacity of the facility). If the fabrication were done at the central facility, the co-located facility would not be needed until the first discharge fuel was ready to be recycled, three years <u>after</u> reactor start-up. This eight-year timing difference can cause significant capital charges that would be repeated for each power plant built. Secondly, if the capacity of the recycle facility's fabrication operation was increased in order to lessen the lead time for the facility the plant would be oversized for recycle operation also leading to economic inefficiency. These penalties would be significantly reduced if the initial core loadings were fabricated at the central LWR reprocessing facility. These options would have to be considered along with other specific decisions about the functions of the two facilities.

4. DEVELOPMENT NEEDS

The base of knowledge of the experts involved in this study and this examination of process and flowsheet options provided a good perspective on the status of technology for the processes described. From this, the initial understanding of the R&D needs required to develop the technology, further

assess the options, and make choices, was gained. We shall briefly describe these development needs. To bring the technology to industrial operation would require a broader plan that bridged from the initial development to future deployment. These initial development needs are explained in more detail in Appendix C. In all the processes we considered, a generic requirement should be to minimize the generation of waste streams that would require long-term isolation. Other primary development needs are listed below.

4.1 AQUEOUS PROCESSES

Development and testing of minor alterations to the PUREX process is needed to maximize the routing of neptunium with the particular products that might be desired (either the plutonium or a separate neptunium product). France has done work along this line associated with their substantial reprocessing activities, and it may be possible to utilize that work as the major source of information. As a minimum, some confirmatory lab- and pilot-scale work in U.S. facilities should also be planned.

The TRUEX process has been developed at ANL and Hanford for removal of actinides primarily from plutonium finishing plant wastes. Development work is needed with wastes containing the spectrum and realistic concentrations of fission products and actinides typical of that from LWR reprocessing.

Many steps in the conversion of nitrate solutions to metal fuel have been done in the past, but only in test or military production programs. Further work is needed here in several areas:

a. Testing and comparing direct thermal denitration with oxalate precipitation processes for conversion of plutonium/neptunium nitrate solutions to oxides.

b. Further analysis and assessment of the processes for converting oxides to metal should be made; such processes have been used at Rocky Flats and at LLNL and are under development for the SIS and AVLIS process.

Actinide/lanthanide separations are difficult by means of aqueous methods, and they have been done only in lab- or small-scale systems. The ANL pyro-process is reported to provide adequate separation. The proposed LTR case depends on the LMR fuel recycle facility for this separation. It must be developed for recycle in any case. Ion exchange and solvent extraction processes have been proposed and some tests done. Further work is required on all these methods before a valid comparison could be made for a process at the scale needed here.

Although not addressed here, the recovery of other long-lived radionuclides (particularly ^{99}Tc, ^{129}I, ^{135}Cs, ^{14}C, and possibly others) must be considered. Of these, only ^{129}I using aqueous processing is well understood.

The aqueous flowsheets which deviate from the LTR case would require more effort to further develop the flowsheets and to better understand options, uncertainties, and costs.

4.2 NON-AQUEOUS PROCESSES

The molten-salt flowsheet that we identified needs cold chemistry tests to verify the chlorination step for UO_2 and a flowsheet analysis, using the scientific literature to identify potential process needs requiring additional study. If the chemical feasibility can be demonstrated, then the engineering issues would have to be evaluated.

The chemistry of the fluoride-volatility process is better understood than that for the molten-salt process; however, it would need extensive testing to assure that all the proposed steps can be operated. We anticipate that the major problems will involve heat-transfer and mechanical problems, such as formation of molten or "sticky" fluoride products.

The programs we envision would address both basic process chemistry and recovery potential. Process choices may be dictated by the required recoveries, depending on the eventual recovery goals determined. Additional R&D may be needed for further special treatment of solid and liquid waste streams to achieve those recoveries. Such programs should follow the initial work.

5. REFERENCES

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2. Leslie Barris, "Rekindled Interest in Pyrometallurgical Processing," Chem. Engr. Progress, pp. 35-39 (February 1986).

3. A. G. Croff, J. O. Blomeke, and B. C. Finney, Actinide Partitioning – Transmutation Program Final Report – I. Overall Assessment, ORNL-5566 (June, 1980).

6. APPENDIXES

APPENDIX A: Scope of Study

A conceptual flowsheet evaluation will be conducted to provide recommended flowsheets for the recovery of transuranium actinides from LWR fuel fission and/or transmutation in an LMR. The evaluation will be performed by a panel of experts selected from ORNL personnel. The evaluation will progress through the following steps:

1. Determine the requirements of the LMR for transuranic feed from LWR reprocessing and the requirements for recycle or disposal of the uranium. This will require consultation with appropriate personnel from outside ORNL.

2. Determine the selection criteria and the relative importance of each. Input will be sought from other LMR program participants.

3. The panel will select promising process steps and flowsheets.

4. The panel will evaluate the process steps and flowsheets using the selection criteria.

5. The panel will recommend the most appropriate flowsheets and prepare a draft report including (a) flowsheets considered, (b) selection criteria, (c) preferred flowsheets, and (d) an outline of a development program required for flowsheet demonstration.

6. A peer review of the draft report will be performed by outside consultants.

7. A final report will be prepared which incorporates comments from the peer review.

APPENDIX B: Additional Discussion on Process Step Options

The various process steps will be discussed in the order in which they would appear in a processing plant: disassembly, removal of the fuel from the cladding, disruption of the cladding to expose the fuel, removal of the fuel from the cladding prior to dissolution, dissolution of the fuel, separation of the uranium from other components, separation of materials other than uranium, separation of fuel components from nitric acid for conversion to a shippable form, and conversion of oxide or chloride to metal.

Process steps were evaluated by the criteria developed. The most desirable process steps, as determined by the evaluation committee are indicated by an "*" preceding its description. Other possibilities which may have merit, but have not been adequately demonstrated, are indicated with a "+".

Disassembly - There is merit in the removal of hardware (especially that constructed of stainless steel, such as end fittings) and disassembly so only fuel pins would be processed. This would decrease the amount of TRU-waste somewhat. Whether this is a desirable option depends on whether the additional mechanical complexity of the system is justified.

Disruption of the Cladding to Expose the Fuel - A number of possible options exist. These are as follows with discussion of advantages and disadvantages.

*1. Decladding with a mechanical shear. This is the standard method and has a large technological base; no development is needed.

2. Perforation of cladding. In this approach a high-power laser perforates or slits the cladding to expose the fuel for further processing. Note that the pins would need to be removed from the fuel bundle before perforation. A Voloxidation step would likely follow the perforation to get better exposure of the fuel materials. This approach would eliminate the use of a mechanical shear, but it would require a more complex handling system. Operability could suffer from difficulty in withdrawing pins from fuel bundles, and bent pins could be difficult to align for perforation. A possible problem is melting of some fuel and alloying of melted fuel with the cladding. Limited hot experience gave a lower grade to the technology base; laser cutting of hardware has been developed and is used in the United Kingdom.

3. Decladding by chemical (ZIRFLEX) or electrochemical dissolution. The waste stream will contain a portion of the actinides requiring additional processing. This is an operating process at INEL and Hanford.

+4. Use high-temperature oxidation/nitriding to destroy the cladding. Although this process has not been operated on a large scale, tests have been made of oxidation/nitriding of Zircaloy-clad thoria for decladding of the fuel. Hot-cell tests have also been made of oxidation of the cladding of LWR fuel for examination of reactor safety issues. Under conditions which would result in oxidation of the Zircaloy, volatilization of fission products was minimal. Laboratory-scale tests have shown that such a treatment does not significantly affect the dissolvability of the plutonium when LWR fuel is oxidized. The fuel is partially oxidized by this treatment leading to some release of volatile fission products. Disadvantages include the use of a high-temperature process and the small information base.

+5. Volatilize the Zircaloy as $ZrCl_4$. This step should be chemically feasible using either Hcl or Cl_2; and, we believe it has been tested with non-radioactive Zircaloy. Numerous problems, or at least questions, exist for this system. If the decladding is done "dry", the large heat of reaction must be accommodated in some way. Any ZrO_2 would not be volatilized. The $ZrCl_4$ is not suitable for a final waste form and must be converted to the oxide; this process would also need development. Some conversion of UO_2 to UO_2Cl_2 could occur in the chlorination step, but this compound has a low volatility. Plutonium and the other actinides should not form volatile compounds. This step would precede dissolution of the fuel in a molten salt. More discussion of the problems and possible approaches are given in Appendix C.

Removal of the Fuel from the Sheared Cladding Prior to Dissolution - Mechanical agitation with or without prior oxidation of the fuel has some potential for removal of the fuel from the sheared cladding.

1. Mechanical agitation of sheared fuel to remove fuel pieces. Reactor fuel pellets are cracked during temperature cycling of the reactor and most of the fuel will fall from the cladding if it is sheared into short lengths and then agitated. Complete separation of the fuel from the cladding (and cladding fragments from the fuel) will likely leave excessive actinide contamination on the hulls; this would require a dissolution step for the hulls for complete removal. The technology base is limited to small-scale work.

+2. Voloxidation and agitation to remove fuel from sheared or perforated cladding. This would remove the bulk of the fuel, but could probably not produce a non-TRU cladding waste without some aqueous step. If simple agitation with an aqueous solution can give an non-TRU cladding this process would be acceptable for a dry flowsheet. On the other hand, if extensive leaching would be required, no advantage over dissolution of the fuel is evident.

Dissolution of the Fuel

*1. Dissolve fuel from sheared cladding using nitric acid. This is the standard process with many years of successful operations.

2. Dissolve fuel from sheared cladding using hydrochloric acid. This step was considered since we thought there could be some advantage to using hydrochloric acid in a flowsheet leading to a chloride product. Later consideration indicates that this is not true. Recovery of a dry uranium chloride from the aqueous chloride solution is difficult, if not impossible. Shipment of a chloride salt will likely be forbidden, due to the solubility of the salt. The chloride waste would be more difficult to handle, although the actinide content may not be high. Dissolution of LWR fuel in hydrochloric acid has not been demonstrated. Dissolution of UO_2 in hydrochloric acid can be

done if an oxidizing agent is present, but the data base is weak. Dissolution of PuO_2 in hydrochloric acid is well established.

3. Dissolve fuel from sheared cladding using a molten salt. There is no information to choose a salt for the purpose. Dissolution of cladding as well as fuel may be a problem.

+4. Dissolve fuel in a molten chloride salt using carbon and chlorine. Literature information states that UO_2 can be dissolved in molten NaCl-KCl eutectic at 860°C using chlorine and a finned block of graphite.[1,2] According to this information, a heel of UCl_4 reacts to dissolve the UO_2. It is not clear whether dense UO_2 can be dissolved in this way or whether the fuel would have to be oxidized and reduced to produce high-surface-area UO_2.

Based on the evaluations of the process steps to this point, the route most assured of working is to shear the fuel element and remove the fuel from the cladding using nitric acid dissolution. A possibly attractive process is high-temperature oxidation which would also be followed by dissolution of the fuel in nitric acid. The chlorination process is also of interest and would lead to a non-aqueous flowsheet. Fluoride volatility flowsheets would not use a dissolution step.

Separation of the Uranium from Other Components - Based on the earlier evaluations, the uranium and other components of the fuel have been dissolved in nitric acid (all aqueous flowsheets), are dissolved in a molten chloride salt, or are processed without dissolution by fluoride volatility. The following are process options and evaluations for separation of the uranium as a clean stream for treatment by enrichment or disposal as a waste:

*1. Solvent extraction using tri-n-butylphosphate (PUREX). This is the standard process and is well developed; the uranium would be cleaned by more than one cycle of solvent extraction to ensure a low-alpha radioactivity product.

2. Separation of uranium using organic ion-exchange. Organic ion-exchange resins might not be practical for use in the high radiation environment.

3. Separation of uranium using inorganic ion-exchangers. This would be an excellent system if an inorganic, anionic ion-exchanger of the proper chemical and physical properties was available. Such a material is currently unknown.

+4. Separation of uranium by pyro-processes. This route would be used if the fuel was dissolved in a chloride salt by chlorination in the presence of carbon.

+5. Separation of uranium by fluoride volatility. This is a well-demonstrated process, but would require extensive development for specific applications. This would be the only separation step used in a fluoride-volatility process.

Separation of Materials other than Uranium - Separations of plutonium from the other actinides and of the actinides and lanthanides from the other fission products could be advantageous.

*1. Use Solvent extraction with tri-n-butylphosphate (PUREX) to separate the plutonium. This is the standard process and is well developed. Neptunium would also be recovered, either separately or with the plutonium.

*2. Use TRUEX or a modification thereof to remove trans-plutonium actinides and lanthanides from other materials. This should be feasible, although the process has not been tested with all the fission products present.

+3. Separations using pyro-processes. This route would be used if the fuel was dissolved in a chloride salt by chlorination in the presence of carbon.

Separation of Fuel Components from Nitric Acid for Conversion to a Shippable Form - The shippable form would likely be oxide or clad metal fuel elements. Soluble compounds are probably not acceptable.

*1. Precipitation of oxalate followed by calcination to oxide. This process is intended for possible use in flowsheets where precipitation of all actinides and lanthanides is desired. This process is well developed for the actinides and has been demonstrated for the HAW of PUREX. Some more effort would be needed to examine the completeness of the precipitation under the proposed conditions.

*2. Direct thermal denitration to oxide as by COPRECAL or denitration in the presence of ammonium nitrate. There is some doubt as to the operability of a direct denitration type of system with all of the fission products present. It is the process of choice where only actinides and lanthanides are present since it requires handling of powder only once (as compared to oxalate precipitation where powder handling is required twice).

Conversion of Oxide or Halide to Metal - If it is decided to ship the product as metal rather than as oxide, a conversion method is needed.

*1. Direct oxide reduction using calcium metal. This method has been demonstrated for plutonium oxide. In the LWR plant the oxide to be reduced would contain other oxides and this would need testing. Uranium and neptunium would be the components of largest concentration other than plutonium. According to Tom Crawford of LLNL, these three components would co-reduce without any problem. If the uranium content is above 30% the melting point of the alloy would exceed 700° C; this would create a significant problem in selection of container materials.

+2. Conversion using pyro-processes. This route would be used if the fuel was dissolved in a chloride salt by chlorination in the presence of carbon. These processes would aim at the production of metals or metal alloys.

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APPENDIX C: Additional Discussion on Development Needs

It appears that neptunium recovery will be a major requirement of any processing flowsheet. In all cases, control of neptunium needs to be developed and/or demonstrated. Neptunium valence control during the solvent extraction steps is the major requirement for its recovery in the aqueous processes and development/demonstration of this control should have the highest priority. This effort could readily be added to existing solvent extraction tests in which valence control is being investigated.

Other areas needing investigation for aqueous processing are:

1. Test TRUEX process with feeds expected in this application.
2. Test oxalate precipitation and calcination with feeds expected in this application.
3. Test methods for management of technetium behavior in the processes and for its recovery. Technetium interferes with the partitioning chemistry of plutonium and other species (particularly tetravalent ones), causes difficulty in diffusion plants in the uranium recycle, and has a long-term risk in repositories.
4. Test direct denitration methods (COPRECAL and denitration in the presence of ammonium nitrate) with feeds expected in this application.
5. Test direct oxide reduction and other proposed metal production processes with the feeds expected in this application.
6. Evaluate further the possible use of inorganic ion-exchangers to determine whether this option is worth pursuing.
7. Evaluate further the possible use of high temperature oxidation of Zircaloy to determine whether this option is worth pursuing.
8. Develop or test processes for recovery of other long-lived radionuclides.

The pyro-process suggested in the paper has basic questions regarding the ability of the proposed process steps to operate successfully. The process requires removal of the Zircaloy as $ZrCl_4$ and then dissolution of the fuel in a molten salt by reaction with carbon and chlorine. Both of these processes are largely undefined and would need considerable work. Some of the options, problems, and development needs are given below for the two main parts of the pyro-process option.

<u>Volatilization of Zirconium</u> - Some work was done at ORNL a number of years ago by Ted Gens to develop a process called ZIRCEX which involved volatilization of the Zircaloy cladding as the chloride. The existing literature should be reviewed to determine the level to which this process was developed, but this has not been done at this time. Problems which are obvious are:

1. If the reaction with HCl or Cl_2 is carried out in a bed of sheared fuel, temperature control will be difficult.

2. Conversion of the $ZrCl_4$ to a suitable form (probably oxide) for disposal is required. Some guidance for this process is available from the titanium industry.

3. If HCl is the chlorination agent, hydrogen will be a product requiring careful handling.

The first problem area could be controlled by hydrochlorination or chlorination using a dilute reagent in an inert gas. This would also assure that the hydrogen level (assuming the hydrogen was removed from any recycle inert-gas stream) was below the explosive limit. Another way of controlling the temperature of the reaction would be to chlorinate (with Cl_2) in the molten salt in the presence of carbon to co-convert the zirconium and fuel to soluble chlorides, with the $ZrCl_4$ probably being volatilized from the salt. The vapor pressures of the species are not known over molten chloride salts. Some fission products, including tritium, will be volatilized and would need control. A literature survey and demonstration of the process using unirradiated Zircaloy and UO_2 should be done.

Conversion of the $ZrCl_4$ to ZrO_2 appears to be very similar to one step of the commercial process for producing pure TiO_2. In that process, $TiCl_4$ is reacted with oxygen at elevated temperature (free energy change ~[-42 kcal (-176 kJ)]/mol) to regenerate chlorine for recycle. The same reaction of $ZrCl_4$ has a free energy change of ~[-39 kcal (-163 kJ)]/mol, and should require similar conditions and equipment. In the titanium process, the chlorine stream which contains some oxygen, is recycled to a fluidized bed of rutile and carbon where $TiCl_4$ is formed. Recycle of the chlorine to react with more Zircaloy would require removal of the excess oxygen and may not be a practical step. Demonstration of this step would have a lower priority than demonstration of the removal of the Zircaloy and dissolution of the UO_2.

Dissolution of the fuel in a molten chloride salt - According to a British patent, high-surface-area UO_2 can be easily dissolved in molten chloride salts by chlorination in the presence of graphite. This would be an attractive process if it will work directly with declad reactor fuel. If it is necessary to oxidize the fuel and reduce it with hydrogen to generate a high-surface-area oxide, the process will be much less desirable. This process should be demonstrated with high-density UO_2.

Both the processes could experience problems with all the fission products present; if the "cold" studies are successful, studies with irradiated fuel could be warranted.

The chloride salt, containing the uranium, actinides, and fission products chlorides, would be processed for recovery of the products by pyrochemical processes analogous to those projected for the IFR or to those currently under development for the AVLIS system. Development and/or demonstration of these processes should not be done unless the basic decladding and dissolution processes are shown to be feasible.

APPENDIX D: Degree of Recovery of the TRU Actinides

In principle, the goals for actinide decontamination, partitioning, and recycling in LMRs should be based upon a balanced assessment that considers the potential biological hazards of various radionuclides, risks associated with disposal in geological repositories, and costs of achieving various degrees of removal from waste streams. For this preliminary study, it was not practical to undertake such a broad systems assessment. However, a simplified calculation model was constructed to provide the study with some perspective concerning the influence of decontamination/partitioning factors on the relative hazards associated with long-lived TRU wastes. The model included:

1. an account of radioactive decay in actinide chains following reactor discharge and reprocessing;
2. consideration of actinide losses to waste streams from reprocessing, plus actinides recycle in LMRs;
3. consideration of relative hazards associated with ingestion of various TRU actinides, reflecting recent reassessments of biological risks consequent to the uptake of specific radionuclides; and
4. an approximate representation of nuclear industrial growth and evolution after commercial deployments of LMRs begin.

The consideration given to relative biological hazards of various TRU actinide elements was based on reassessments made during the past decade by the International Commission on Radiological Protection (ICRP), of cancer-causing propensities for plutonium and other TRU actinides in animal ingestion.[1,2] Some implications of the 1979 ICRP reassessment (Ref. 1) for evaluating the biological hazards of high-level radioactive wastes were examined and reported in 1982 by B. Cohen.[3] Figure D-1, part of the preliminary background information provided for this study, shows the "radiological risk factor" associated with spent LWR fuel versus time after reactor discharge. Figure D-1 is derived from Cohen's analysis.[3] The "risk factor" appearing as an ordinate in the graph has been normalized to unity for the uranium originally mined to produce the LWR fuels.

As discussed by Cohen, the ICRP 1979 assessment reflected an expansion in knowledge concerning animal metabolism of various radionuclides compared with earlier ICRP publications. In particular, it was noted that estimates of relative biological hazards for ^{237}Np (half-life, 2.1 million years) were significantly higher (factor of 144) than in earlier estimates and, to a lesser degree, hazards for ^{241}Am and ^{243}Am (half-lives 460 years and 7950 years, respectively) were also higher. The hazards for all actinide elements including uranium were increased, but by widely

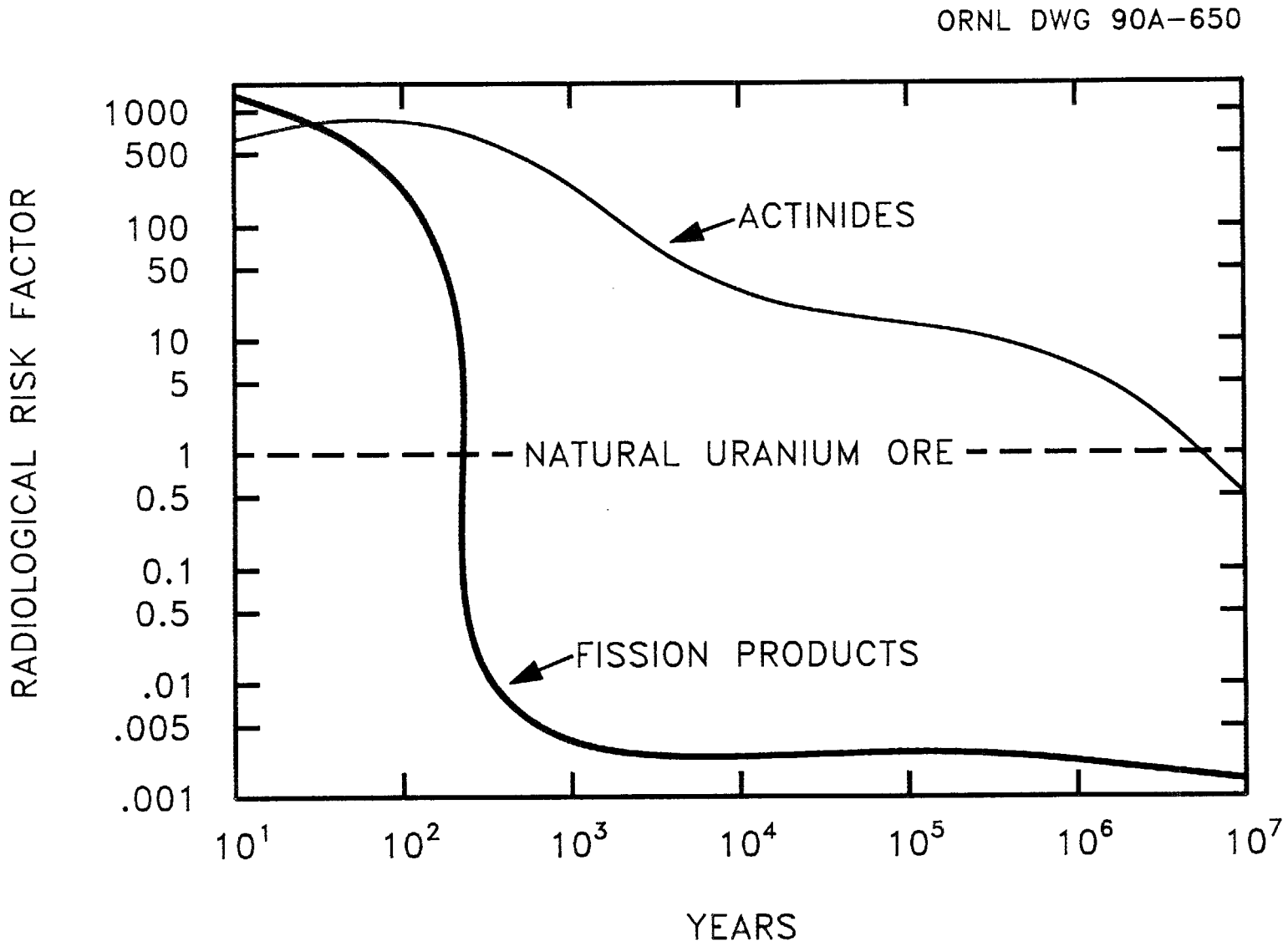

Fig. D.1. Radiological risk without actinide removal.

varying factors. The analysis reported by Cohen, based upon ORIGEN-2 calculations for LWR spent fuel and reprocessing wastes, indicated that the most hazardous TRU nuclides were ^{241}Am at 10^3 years; ^{243}Am, ^{239}Pu, and ^{240}Pu at 10^4 years; and ^{237}Np beyond 10^5 years. The analysis also showed that the hazards in the spent fuel at 10^3 years would be about two orders-of-magnitude above that of the uranium originally mined to produce the LWR fuels (actinide hazards associated with decay chains of ^{238}U and ^{235}U) and would become roughly equivalent at 5 million years.

Issues concerned with the evaluation of biological hazards of various radionuclides are quite complex and subject to continuing analyses and refinements. As an indication, in 1986 the ICRP adopted and published an updated assessment of information relating to animal ingestion and metabolism of various TRU actinides.[2] In that publication, several changes in recommendations were given, relative to those resulting from the 1979 assessment. Most significantly, the estimate of the effective fractional absorption of ^{237}Np into the blood stream from the GI tract (required for bone and liver deposition) was reduced by a factor of ten, thereby reducing the estimated hazards for neptunium by about an order-of-magnitude. Also, estimates of the hazards associated with long-lived isotopes of plutonium, relevant to population exposure via food chains, were increased by a factor of ten. (Specifically, annual limits of intake of unknown or mixed compounds containing plutonium were reduced by almost a factor of ten compared to ICRP Publication 30.)

Other than to note the changes in these official recommendations during the past decade and the general trend toward higher estimates of biological hazards associated with animal uptake, this study is insufficient to provide recommendations concerning the "absolute" hazards or risks to be assessed to various actinide elements for evaluating strategies for partitioning and burning. There are several reasons for this conclusion. The relative hazards or risks associated with ingestion or inhalation of these elements depends on the scenario assumed for migration to the biosphere, which is left out of this analysis. The relative hazards estimated in Cohen's analysis and in the analysis given below were based on ingestion of nuclides in the relative concentrations present in the original waste material placed in the repository, with account taken for radioactive decay over time. However, factors such as the chemistry of a specific site could, over very long periods, result in separation of various elements in any ground water elution scenario. In this context, there is some evidence that ^{237}Np could be of special significance because of its relatively high ion mobility.[4] In general, the combined removal/radioactive decay that occurs during migration can cause order-of-magnitude changes in what is important, and any hazard indexes cannot readily account for this. Thus, depending on the ground rules used, the risk factors associated with spent LWR fuel waste (the reference case for this analysis) could be higher or lower than indicated in Fig. D-1.

It is important to emphasize that there are good reasons for expecting that the actual risks associated with placement of the long-lived TRU actinides in repositories would be very small for any of the relative "weights" assigned to biological hazards considered here. [Note: here, "risk" is considered to be proportional to the product of the probability of a specific release event times the potential consequence (hazards).] Risk assessment involves a number of considerations beyond the scope of this study, and the analysis of relative waste hazards discussed here should not be interpreted as a risk assessment.

Recognizing these caveats, some rough estimates were made of the possible significance of assigning different relative weights to the hazards of various TRU nuclides, accounting for the fact that they decay at different rates and could potentially dominate the biological hazards at different times. As explained above, any possible effects of chemical separations among these elements over time were ignored. Two different sets of assumptions were considered for this analysis:

Case A: Hazards directly proportional to radioactivity (curies),

Case B: Hazards weighted according to the 1982 assessment reported by Cohen,[3] which was based on 1979 ICRP recommendations,

Case A assigns equal propensities for biological uptake among the various isotopes of plutonium, neptunium, and americium, and assumes that biological hazards are strictly proportional to radioactivity. Case B reflects higher relative hazards for ^{237}Np and americium than plutonium for equal sources of radioactivity. It is noteworthy that case A is in rough accordance with the 1986 ICRP recommendations when the order-of-magnitude reduction in neptunium hazards is combined with the estimated order-of-magnitude increase in plutonium hazards for general population exposure by ingestion.

The results of calculations made with the simplified model referred to earlier are summarized in the remainder of this appendix. Several explanatory notes needed in interpreting these results are as follows:

1. The numerical values (indices) for actinide hazards listed in the tables were calculated in relative terms, using unreprocessed spent LWR fuel as a reference basis. The long-term hazards are expressed in terms of two indices, one based on the actinide concentrations existent at 1000 years after discharge (denoted by 10^3 in tables) and the other based on time-integrated hazards for 1000 years and beyond denoted by 10^{3+}). This second index is perhaps the more significant and can be interpreted as a crude measure of potential hazards under a scenario wherein there was gradual uniform leakage from a repository over a very long time period, starting about 1000 years after emplacement (roughly the time when the integrity of engineered containment for the wastes could no longer be guaranteed). The first index is the corresponding crude measure of relative hazards present in the wastes at the beginning of this decay period.

2. Two sets of assumptions concerning the relative biological hazards of various TRU actinides were considered (cases A and B referred to above).

3. In these calculations, decontamination factors were expressed in terms of net fractions of various actinides processed that go into waste streams (i.e., not recycled). Two cases were selected for the illustrative calculation in the tables:

   (a) Waste fractions 0.005 for Pu, Np, and Am, for both LWR and LMR fuels reprocessing;

   (b) LWR waste fractions 0.005 for Pu, 0.05 for Np and Am: LMR waste fractions 0.001 for all TRU actinides.

   These choices were somewhat arbitrary but sufficient to indicate the sensitivity to Np and Am partitioning and decontamination in the LWR reprocessing/conversion step.

4. The actinides recovered from LWR reprocessing, to be supplied as initial LMR fuel inventories, were calculated according to specified decontamination and partitioning factors for the LWR recovery step. The average period of interim storage of spent LWR fuel prior to reprocessing was assumed to be 10 years. For LMR recycle, rough approximates were used for the effects of continuing recycle and burnup of the actinides. The burnup of ^{237}Np was explicitly accounted for in the computing algorithm; however, inventories of all other TRU actinides were assumed to remain in approximate equilibrium, with production roughly balanced by burnup.[4]

Some results of these calculations are summarized in Tables 1A and 1B. These list the long-term hazard indexes associated with three different waste forms: (1) LWR spent fuel for direct disposal (the reference case); (2) reprocessed LWR fuels; and (3) reprocessed LMR fuel. The tables list the calculated total hazard indexes for the two sets of decontamination assumptions (Cases a and b referred to above), followed by the proportions of the total hazards associated with various nuclides. As expected, the proportions calculated for the two hazards weighing schemes differ. It is noteworthy, however, that the magnitudes of the total hazard indexes are roughly similar when expressed relative to spent LWR fuel (hazard index = 1), indicating that overall hazards might not be highly sensitive to the weighing scheme used.

These calculations illustrate the basic point that reprocessing LWR fuel could reduce potential long term hazards from TRU nuclides in repository wastes by about two orders-of-magnitude, even with relatively modest efficiencies for recovery of neptunium and americium [compare cases (a) and (b) in these tables]. They also suggest that a potential evolution could occur over time in the residual actinide waste hazards from LWR and LMR fuels, with more efficient actinide recovery in the latter fuel tending to compensate for possibly less efficient recovery in LWR fuel reprocessing.

While the hazard indexes listed in Tables 1A and 1B are internally consistent, each normalized to unity for unreprocessed LWR fuel, it is important to note that the hazard indexes for the two weighing schemes (A and B) differ relative to each other. The calculated magnitudes of the indexes for spent LWR fuel (the reference base) for weighing scheme B, relative to unity for

Table 1A: Relative hazards from TRU actinides in radioactive wastes, calculated for 1000 years and beyond

(Basis: 1 kg HM in discharged spent fuel)

	Direct disposal of spent LWR fuel		Reprocessed wastes LWR fuel		Reprocessed wastes LMR fuel	
(a) Waste Fractions: 0.005 for all TRU Actinides; LWR and LMR Fuels						
Years:	10^3	10^{3+}	10^3	10^{3+}	10^3	10^{3+}
Relative hazards:	1.0	1.0	0.0079	0.0071	0.0519	0.0487
Distribution (%):						
^{239}Pu	19.68	52.51	12.52	37.19	18.65	52.99
^{240}Pu	30.75	22.13	55.96	44.85	34.40	26.37
^{242}Pu	0.09	3.61	0.06	2.56	0.08	3.64
^{241}Am	48.44	2.43	30.80	1.72	45.89	2.45
^{243}Am	0.98	0.85	0.62	0.60	0.93	0.86
^{237}Np	0.07	18.47	0.04	13.08	0.05	13.69
(b) Waste Fractions: LWR fuel, Pu = 0.005; Np; Am = 0.050 LMR fuel, Pu, Np, Am = 0.001						
Years:	10^3	10^{3+}	10^3	10^{3+}	10^3	10^{3+}
Relative hazards:	1.0	1.0	0.0176	0.0135	0.0126	0.0114
Distribution (%):						
^{239}Pu	19.68	52.51	5.59	19.51	15.38	45.44
^{240}Pu	30.75	22.13	24.99	23.53	46.67	37.19
^{242}Pu	0.09	3.61	0.02	1.34	0.07	3.12
^{241}Am	48.44	2.43	66.47	4.36	37.12	2.06
^{243}Am	0.98	0.85	2.78	3.17	0.73	0.70
^{237}Np	0.07	18.47	0.14	48.10	0.04	11.48

Table 1B: Relative hazards from TRU actinides in radioactive wastes, calculated for 1000 years and beyond

(Basis: 1 kg HM in discharged spent fuel)

	Direct disposal of spent LWR fuel		Reprocessed wastes LWR fuel		Reprocessed wastes LMR fuel	
(a) Waste Fractions: 0.005 for all TRU actinides; LWR and LMR fuels.						
Years:	10^3	10^{3+}	10^3	10^{3+}	10^3	10^{3+}
Relative hazards:	1.0	1.0	0.006	0.0051	0.0497	0.0367
Distribution (%):						
^{239}Pu	6.72	2.31	5.62	2.27	6.65	3.09
^{240}Pu	10.50	0.972	5.14	2.74	12.27	1.54
^{242}Pu	0.03	0.16	0.02	0.16	0.03	0.21
^{241}Am	78.40	0.51	65.58	0.50	77.59	0.68
^{243}Am	1.59	0.18	1.33	0.17	1.57	0.25
^{237}Np	2.76	95.87	2.31	94.16	1.90	94.24
(b) Waste fractions: LWR fuel, Pu = 0.005; Np, Am = 0.05 LMR fuel, Pu, Np, Am = 0.001						
Years:	10^3	10^{3+}	10^3	10^{3+}	10^3	10^{3+}
Relative hazards:	1.0	1.0	0.0226	0.0341	0.0106	0.0073
Distribution (%):						
^{239}Pu	6.72	2.31	1.49	0.34	6.26	3.12
^{240}Pu	10.50	0.97	6.65	0.41	18.99	2.56
^{242}Pu	0.03	0.16	0.01	0.02	0.03	0.22
^{241}Am	78.40	0.51	83.86	0.36	71.58	0.67
^{243}Am	1.59	0.18	3.51	0.26	1.41	0.23
^{237}Np	2.76	95.87	4.48	98.61	1.74	93.19

scheme A, were 2.9 for the thousand-year (10^3) index and 22.7 for the time-integrated (10^{3+}) index. As indicated earlier, these comparisons reflect higher biological hazards estimated for ^{237}Np and the americium isotopes, relative to plutonium in scheme B. The influence of ^{237}Np is particularly pronounced in the time-integrated index (10^{3+}) for case B. Note, again, that only the different relative half-lives and biological hazard weights are reflected in these comparisons. They do not constitute a complete assessment of the risks (relative or absolute) associated with placement of the TRU nuclides in repositories.

The calculational model used for these evaluations also included an approximate representation of the "system dynamics" for a two-sector nuclear industry consisting of LWRs and advanced LMRs. Preliminary results can be given a qualitative description here. They indicate that, if the nuclear power industry were to take on a new growth phase, possibly sometime early in the next century, the deployment of advanced LMRs could allow the recovery and effective utilization of the TRU actinides, including plutonium, from LWR spent fuel, with gradual take-down of the stored backlog of this fuel. The long-term actinide hazards associated with un-reprocessed spent LWR fuel tend to continue to dominate those associated with reprocessing waste streams, well after the latter is initiated. Hence, there could be a difficulty in installing LMRs rapidly enough to make any dramatic or short-term impact on the spent fuel backlog now destined for repositories. This would depend somewhat on the rate of future industrial growth. However, it also appears that, if a feasible LMR installation scenario were combined with a strategy of holding spent LWR fuel in dry storage (either at reactors or in an MRS facility) during a relatively long period (e.g., 50 to 100 years), actinide burning in LMRs might make a real impact on "capping" the LWR fuel backlog and reducing the long-term hazards from wastes placed in repositories. These issues would need to be considered in any broader "systems study" of LWR/LMR fuel cycle configurations, but they are beyond the scope of this discussion.

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APPENDIX E: Recovery of Long-Lived Fission Products

The scope of this study was limited primarily to the behavior of the actinide elements. The ramifications of several other long-lived radioisotopes should be considered in the context of their long-term (>1000 years) impact on risks. By the same logic, toxic stable elements should also be included; however, they have not been considered in this phase of the study. These risks may be orders of magnitude smaller than those from residual actinides. Radioactive isotopes include ^{14}C, ^{59}Ni, ^{99}Tc, ^{107}Pd, ^{129}I, ^{135}Cs, and possibly a few others. The need for dealing with these radionuclides, and methods that might be used should there be a need, are beyond the scope of this study. However, a brief estimate of where they would go during reprocessing is given here. Part of the ^{14}C and nearly all the ^{129}I can be recovered from the dissolver off gas and dealt with in some manner. The rest of the ^{14}C would be associated with undissolved cladding and fuel hardware, as would be all of the nickel; and this would not reasonably be involved in the partitioning/transmutation (P/T) processes. Technetium would distribute between the HAW and actinide products in the solvent extraction operations, depending on flowsheet details; thus, its behavior is subject to manipulation and it must be considered in the context of P/T processing. Palladium would distribute between the dissolver insolubles and the HAW, mostly the latter; it could be dealt with by treating those fractions. Cesium will follow the HAW unless it is recovered (probably along with strontium) to reduce the heat load over the time frame of several decades. Of these radioisotopes, only technetium is substantially affected by the processing that would be appropriate in any case, and its behavior will have to be considered in some detail in the next stage of this study. Technetium is especially important because it can cause a deleterious effect on certain reductive partitioning processes for plutonium separation. Palladium, along with other noble metals, has been considered as a possible candidate for recovery. Of the actinides, neptunium can split between several streams (like technetium), or be recovered as a separate product. Thus, technetium and neptunium are the two elements that are most affected by processing options (aside from uranium and plutonium which are the primary objectives); and these two must be evaluated in follow-on flowsheet studies.

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